

A simulation study on selection of optimized process for azeotropic separation of methanol and benzene: Internal heat integration and economic analysis

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Abstract—This work provides an insight into the separation of azeotropic mixtures by using two different techniques: pressure swing distillation and extractive distillation. Both methods are used to separate an azeotropic mixture of methanol and benzene. This mixture exhibits a minimum boiling azeotrope at temperature 57.97 °C and pressure 1 bar with mole fractions of 0.61 and 0.39 for methanol and benzene, respectively. However, the azeotropic point in methanol and benzene mixture is pressure sensitive, which can be shifted by changing pressure with a process called pressure swing distillation. Extractive distillation with suitable solvent is another method to separate such kind of mixture. Both methods are rigorously simulated and optimized for minimum heat duties. Internal heat integration is applied too for increasing energy efficiency. New optimization techniques are carried out with process simulator Aspen HYSYS V8.4 and results reveal the best method for separation of methanol and benzene azeotropic mixture.

Keywords: Azeotrope, Pressure Swing Distillation, Extractive Distillation, Internal Heat Integration, Solvent

INTRODUCTION

Distillation is widely used in the chemical industry for separation of vital components, and it has been one of the most expensive methods over the time. In spite of its high energy demands, its use is inevitable due to separation demand of chemical mixtures. The high energy demand of distillation columns can be estimated from the fact that reboilers alone consume over 50% of all energy available for heat exchange [1]. Hence, the distillation process is widely considered for optimization and improvements as it can decrease energy requirements up to 70% leading to a tremendous profit [2]. Methanol and benzene azeotropic mixture is widely encountered in the pharmaceutical industry, and this aromatic-aliphatic alcohol mixture is widely needed to be separated to use the potential components in industrial applications. The separation of methanol-benzene mixture has been studied previously only by pervaporation method. However, the pervaporative method for separation of alcohol from aromatics is not an advanced technique due to some limitations, as there is lack of a suitable membrane for a particular individual component [3]. Moreover, hydrophilic membranes have been analyzed in the pervaporative method to separate alcohol from aromatics, but the condition of feed mixtures was restricted up to only 50 vol% methanol with benzene [3,4]. Hence, due to the aforementioned limitations, there is immense need to further study this particular azeotropic mixture of methanol and benzene to get pure alcohol and aromatics.

Conventional distillation is based on the relative volatility to separate the different components, while an azeotrope is generated when the components have low relative volatility [4]. The azeo-

trope creates distillation boundaries and the residue curve cannot cross these boundaries. Hence, distillation regions are generated which exhibit that the components lying in two different regions cannot be separated. Azeotropic separation can be carried out by extractive distillation process, which makes use of an entrainer (solvent) [5]. The solvent added increases the relative volatility of components, and light component can be recovered from the top of the column and solvent along with heavy component goes down to bottom of column. The second column (solvent recovery column) is used to further separate the heavy component and the solvent. The recovered solvent is recycled to the first column, which basically serves as an extractive distillation column [6]. The solvent selection is a very important step in extractive distillation where the separation efficiency and purity depends on the characteristics of solvent used [7-9]. The solvent should have higher boiling point to ensure it being the heaviest component and is capable of modifying the relative volatilities of both components. It should have high selectivity for one of the components and should not make an azeotrope with any of the components to avoid the ternary azeotrope, which will rather make the process more complex. The effectiveness of solvent can be analyzed by the use of residue curve maps which are essential to design the distillation processes [10].

Pressure swing distillation (PSD) works on the concept that the azeotropic point can be shifted by changing pressure. It uses two distillation columns operated at two different pressure values to break the pressure sensitive azeotrope [11-13]. For the minimum boiling azeotropic mixture, the top product from first column is fed to the second column after changing pressure and the pure products are recovered from bottom streams of both columns. An immense research has been done on pressure swing distillation process based on batch [14-16] and continuous systems [17-19]. A new double column batch pressure swing distillation process has been studied extensively by Modla and Lang [20,21]. Both PSD and ex-

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tractive distillation are competitive regarding separation of azeotropic mixtures, and these methods have been studied and compared in past literature [22-25]. Luyben reported the comparison of extractive distillation and pressure swing distillation process for acetone-methanol by using water as solvent. He found that pressure swing distillation provided high purity as the extractive distillation had a trace amount of solvent with the products which was due to vapor liquid equilibrium of components. His study included optimization for column stages and reflux ratio while keeping specific values for top and bottom stream compositions [25].

The close boiling mixtures can be separated by extractive distillation process, first studied by Rabdall and Webb [26]. Extractive distillation process has vast industrial applications [27-29] and it has also been studied for the separation of organic and volatile components [30,31]. The continuous extractive distillation process has been studied [32-35], and the separation by extractive distillation has been improved and investigated [36,37]. Dehydration of ethanol mixtures by extractive distillation has been studied by Black and Ditsler [38]. The other work by Hilal et al. includes reduction of solvent used for optimum consumption [39].

The distillation process can be made more energy-efficient with the help of external and internal heat integration. The external heat integration, such as VRC (vapor recompression), makes use of a compression system which renders the process more complex and energy demanding. Therefore, internal heat integration can be used for an economically attractive process [40]. In a simple heat integrated distillation column (HIDiC), heat transfer occurs from rectifying to stripping section. But in internal heat integrated PSD process (IHIPSD), the process follows the basic principles of conventional PSD process which makes IHIPSD a different process than HIDiC. The PSD process has different temperatures depending on different pressure in both columns; hence, this temperature difference creates the possibility of internal heat integration in the PSD process. Internal heat integration, first proposed by [41], has been studied by various researchers [42,43]. By internal heat integration resulting from temperature driving force, the heat from high pressure (HP) section of the column can be transferred to low pressure (LP) section to provide vapor boilup. By such a combination of both columns, the condenser in HP column and reboiler in LP column can be omitted, which makes the process economically attractive. This type of internal heat integration is named as full internal heat integration. On the other hand, partial heat integration [44] utilizes reboilers and condensers in both columns as the energy requirements cannot be completely met from HP section.

To date, the separation of methanol and benzene by pressure swing distillation and extractive distillation has been neglected, and there is no design data available for the corresponding system. A simulation study for methanol benzene mixture has never been carried out and this leads to the lack of design conditions and simulation data along with information about suitable solvent for methanol and benzene. A detailed optimization procedure regarding column sequences in PSD process is absent too in previous studies. Furthermore, internal heat integration is hardly dealt with in simulation studies due to converging issues and increased complexity of the process; hence, the simulated flow sheets for internal heat integration are rare in past literature and most of the past

studies have implemented internal heat integration in HIDiC pilot plants [44,45]. The present study investigated the behavior of azeotropic mixture while using two different methods of azeotropic separation: PSD and extractive distillation process. The pressure sensitivity was analyzed first so that pressure swing distillation can be used. It was found that methanol and benzene azeotrope can be shifted by changing pressure. Availability of a suitable solvent is essential for a specified mixture in extractive distillation process. Hence, a solvent was selected for the optimum configuration of the process based on residue curve maps. The rigorous simulation for both processes was done by Aspen HYSYS process simulator V8.4. First, NRTL thermodynamic model was used to predict the binary interaction parameters by regressing the experimental vapor liquid equilibrium data. The optimized binary interaction parameters are reported. The optimal column sequence in PSD was also found by optimizing reflux ratio and feed stage location in both columns. Corresponding flowsheets were also optimized and the optimum variables reported for both processes. In this study, successfully simulated flowsheets for partial and full heat integration were also generated and unique configurations proposed for optimal results.

SELECTION OF SOLVENT

As the extractive distillation needs a solvent for complete separation of the two components, the selection of a suitable solvent is very important. The solvent shifts the azeotrope to the corner of high boiling component and finally the pure components are recovered. For the concerned azeotropic mixture of methanol and benzene, a thorough study from literature considering solubility, homologous characteristics and hydrogen bonding shows that aniline is the most promising solvent for the separation as it is from the same homologous group as benzene (Robbins chart; Perry's handbook) and has good solubility for benzene [46,47].

Residue curve maps analyze whether a desired purity, while using a particular solvent, can be achieved or not [10]. Residue curve maps are basically triangular diagrams which are used to describe equilibrium relationships. Residue curve map consists of stable node, unstable node and saddle point. The stable node is the point where all residue curves terminate and it represents a component or azeotrope with highest boiling point. The unstable node represents the component or azeotrope with lowest boiling point, while the saddle denotes the pure components and azeotropes having boiling point between stable and unstable nodes. The residue curves originate from unstable point, move towards the pure components, i.e., saddle and then all curves terminate at stable point. The azeotropic mixture of methanol-benzene exhibits the minimum boiling azeotrope at 57.97 °C while boiling points of methanol and benzene are 65.53 °C and 80.13 °C, respectively. The residue curve map of methanol-benzene-aniline drawn in Aspen Plus V8.4 is shown in Fig. 1 and it portrays an effective separation with stable, unstable nodes and saddle points. By observing residue curve map, aniline can be considered as a convincing solvent to separate methanol and benzene.

TXV diagrams for aniline with either of the components have been analyzed by using Aspen HYSYS v8.4. It can be noticed from Figs. 2 and 3 that aniline does not make further azeotropes with

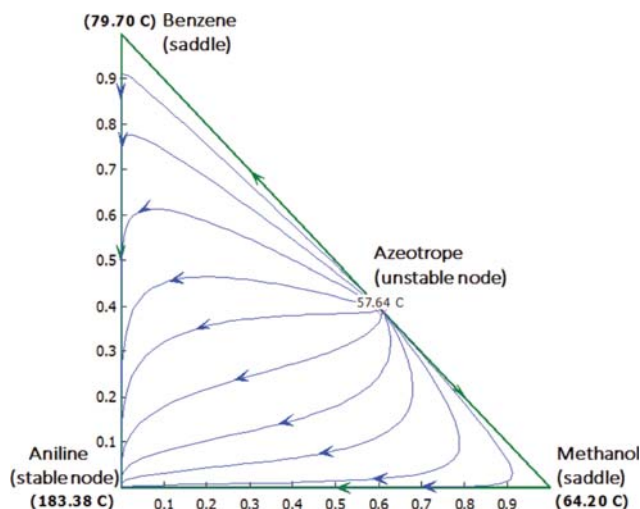


Fig. 1. Residue curve map for methanol-benzene azeotropic mixture and aniline as an entrainer (solvent).

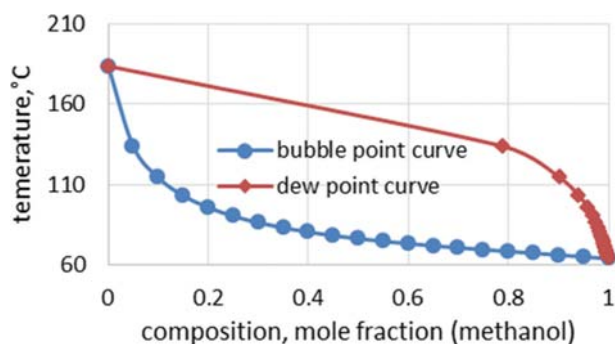


Fig. 2. TXY diagram for methanol and aniline at 1 bar.

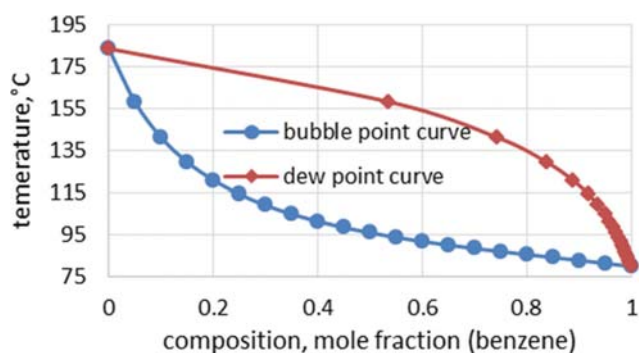


Fig. 3. TXY diagram for benzene and aniline at 1 bar.

either of the two components, which makes the process feasible. Methanol is recovered from distillate as it is naturally more volatile, while aniline leaves from bottom along with benzene. The solvent recovery column is further used to finally achieve 99% purity of each component.

THERMODYNAMIC DATA AND THEORY

Following equations are used to calculate vapor-liquid equilib-

rium:

$$\hat{f}_i^v(T, P, y_i) = \hat{f}_i^l(T, P, x_i) \quad i=1, 2, \dots, n \quad (1)$$

$$\hat{f}_i^v(T, P, y_i) = \phi_i^v y_i P \quad \text{for vapor phase} \quad (2)$$

$$\hat{f}_i^l(T, P, x_i) = \gamma_i x_i P_i^{\text{vap}} \quad \text{for liquid phase} \quad (3)$$

where \hat{f}_i^v and \hat{f}_i^l are chemical fugacities of component i in the vapor and liquid phases, respectively. In this study, Peng-Robinson equation of state and NRTL [48,49] liquid activity coefficient model are used to calculate the fugacity coefficient in the vapor and liquid phases, respectively.

$$P = \frac{RT}{v-b} - \frac{a_c \alpha}{v(v+b) - v(v-b)} \quad (4)$$

$$a = 0.46724 \frac{R^2 T_c^2}{P_c} \quad b = 0.07780 \frac{RT_c}{P_c}$$

$$\alpha = [1 + (0.37464 + 1.64226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad b = \sum_i x_i b_i$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad k_{ij} = 0$$

Eqs. (5) and (6) express NRTL liquid activity coefficient model of component "i".

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right) \quad (5)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad \tau_{ij} = \alpha_{ij} + \frac{\beta_{ij}}{T} \quad (6)$$

Figs. 4, 5 compare the predicted vapor liquid equilibrium (NRTL liquid activity coefficient model) to experimental vapor liquid equilibrium (VLE) data [49] for azeotropic mixture of methanol and benzene.

The three binary interaction parameters of NRTL model (α_{ij} , β_{ij} , β_{ji}) are determined by regression of VLE data for the methanol and benzene system. Table 1 enlists the optimized NRTL binary

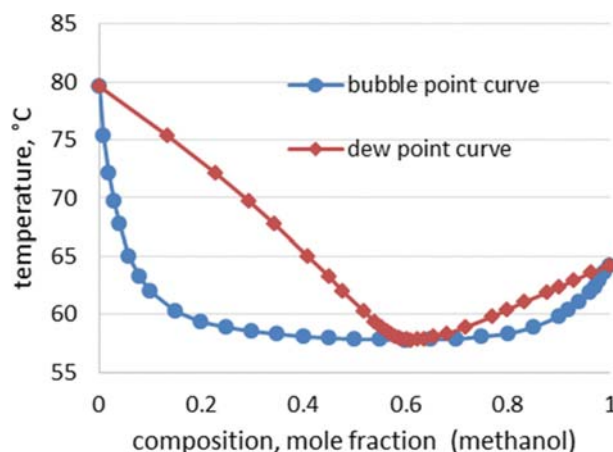


Fig. 4. TXY diagram for methanol-benzene system at pressure 1 bar and comparison of predicted VLE data to experimental VLE data.

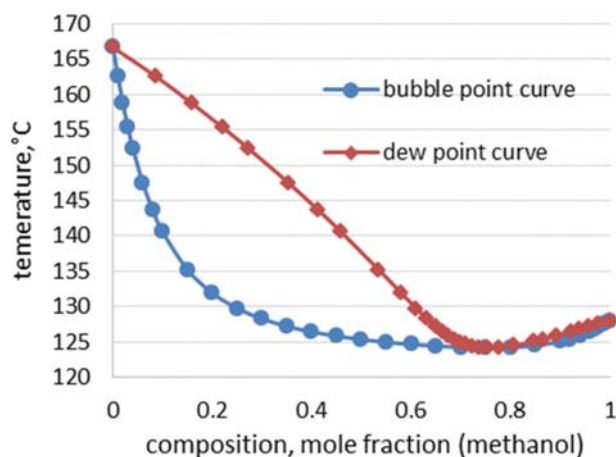


Fig. 5. TXY diagram for methanol-benzene system at pressure 8 bar and comparison of predicted VLE data to experimental data.

Table 1. Optimized NRTL binary interaction parameters

Component i	Component j	α_{ij}	β_{ij}	β_{ji}
Methanol	Benzene	0.47	360.29	567.76
Average absolute deviation		0.0005		
Root mean square deviation		0.0002		

parameters.

The average absolute deviation and root mean square deviation, reported in Table 1, show a very small deviation from the values predicted by NRTL model. Eq. (7) is the expression of objective function for optimizing NRTL binary parameters which are used for phase equilibrium calculations in process modeling and optimization.

$$OF = \sum (\sum (1.0 - Y_{ij,cal}/Y_{ij,exp})^2 + (1.0 - T_{ij,cal}/T_{ij,exp})^2) \quad (7)$$

where $T_{ij,cal}$, $T_{ij,exp}$ denote experimental and calculated dew point temperatures.

PROCESS MODELING, SIMULATION AND OPTIMIZATION

1. Pressure Swing Distillation

The feed conditions for pressure swing distillation process are estimated by pressure sensitivity on methanol azeotropic composition. The azeotropic composition for methanol at varying pressure values is taken from Aspen Plus V8.4 and azeotropic composition is plotted against corresponding pressure and temperature values as shown in Fig. 6. The variation of pressure significantly changes the azeotrope composition. The larger composition shifts lead to less recycle flow rate and energy requirements. Hence, selecting a higher pressure in high pressure column is appropriate for an optimum process [27]. But a very high value pressure leads to incompatibility with the heating system of process; hence, a medium range pressure value is used which provides an appropriate temperature difference across reboiler and results into lower energy requirements. In this simulation study, low pressure (LP) column

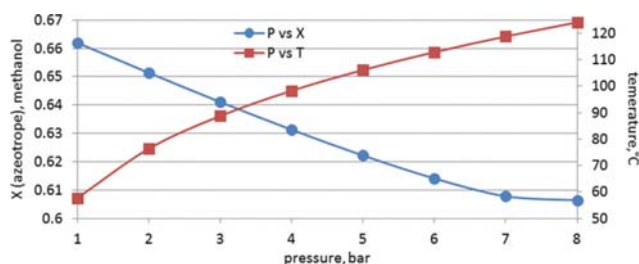


Fig. 6. Azeotropic composition of methanol vs temperature and pressure.

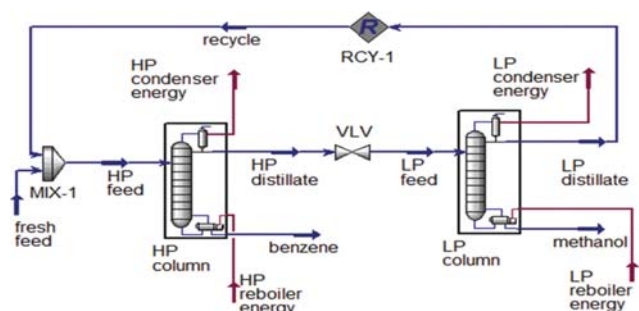


Fig. 7. Pressure swing distillation process flow sheet with inverted column sequence HP-LP.

and high pressure (HP) operate at pressure 1 and 8 bar, respectively. In case of LP-HP sequence, feed is entered to low pressure column, hence the feed composition and temperature can be found by the “P vs X” and “P vs T” curves against pressure 1 bar. In the inverted sequence, HP-LP, the azeotropic composition and temperature can be found against pressure 8 bar. For 1 bar, the composition and temperature of feed is 0.66 and 57.64 °C, while for 8 bar, the composition and temperature found from Fig. 6 are 0.61 and 124.14 °C, respectively.

Fig. 7 shows the process flow diagrams for pressure swing distillation process simulated by Aspen HYSYS V8.4. This process, operating on two different pressures, has high pressure (HP) and low pressure (LP) column. The column sequence, HP-LP, is shown in Fig. 7 which operates with high pressure column first in sequence. Feed is entered to HP column at 8 bar and 99% benzene is recovered from bottom of HP column. HP distillate, after reducing the pressure to 1 bar, is introduced to LP column and 99% pure meth-

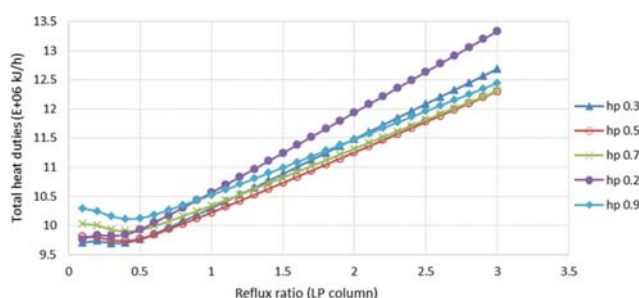


Fig. 8. Reflux ratio optimization for column sequence HP-LP in PSD process.

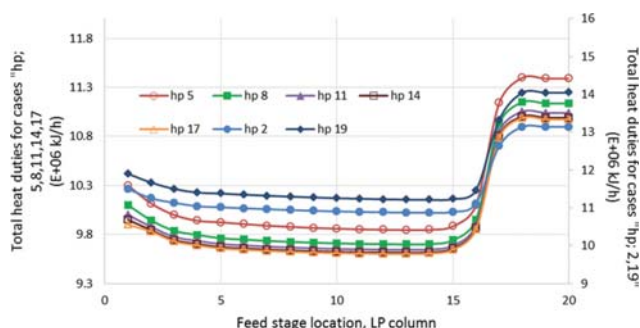


Fig. 9. Feed stage optimization for column sequence HP-LP in PSD process.

anol is recovered from LP bottom. The inverted sequence, LP-HP, is also analyzed to check the optimum sequence for minimum total heat duties.

Figs. 8 and 9 show reflux ratio and feed stage optimizations, respectively, for the HP-LP sequence using high pressure column first in sequence followed by low pressure column. The optimization shows the optimum total heat duty, at reflux ratio of 0.3 in both columns, is $9.69 \text{ E}+06 \text{ kJ/hr}$. Hence, the found optimum value of reflux ratio is fixed in both columns to get optimized variables. Feed stage optimization is also done with varying feed stage locations in both columns and various cases are shown in Fig. 9.

Feed stage in one column is kept fixed while changing feed stage location in other column. The optimum feed stage in hp-lp sequence

is found when feed is introduced to HP and LP columns at stages 17 and 13, respectively. The minimum heat duty in this case is $9.60 \text{ E}+06 \text{ kJ/hr}$. The other combinations of feed stages are found to be expensive as the heat duties get increased gradually. Hence, in HP-LP sequence, feed location is fixed at stages 17 and 13 in HP and LP column, respectively. Moreover, the inverted sequence, LP-HP, is also analyzed and optimization is done on the basis of reflux ratio and location of feed stage. The optimum reflux ratio in LP-HP sequence is found to be 0.5 in LP column and 0.3 in HP column. The feed stage optimization shows that the optimum total heat duty can be achieved by fixing feed location at stage 14 and 16 in LP and HP columns, respectively. The optimum heat duties exhibited by LP-HP sequence are $1.123 \text{ E}+07 \text{ kJ/hr}$ and $1.121 \text{ E}+07 \text{ kJ/hr}$ for sensitivity analysis of reflux ratio and feed stage location, respectively. The optimized simulation results for PSD process are listed in Table 2. The optimization work proves that the HP-LP sequence is better than LP-HP sequence in terms of energy requirements. Therefore, further optimization based on heat integration will be applied on HP-LP sequence.

2. Extractive Distillation

Fig. 10 depicts a process flow diagram for extractive distillation which operates with two distillation columns. The first column used in the process is extractive distillation and the second column is solvent recovery column. The feed, containing methanol and benzene mixture, is fed to the first column to undergo boil up for separation. As a result, the light component is collected in the top of column as distillate and the less volatile component is collected in

Table 2. Simulation results for PSD process

	Temperature C	Pressure bar	Molar flow kgmole/h	Composition (mole fraction)	
				Benzene	Methanol
Fresh feed	125.00	8	100	0.5	0.5
HP feed	124.98	8	263.51	0.41	0.59
HP distillate	123.85	8	213.30	0.33	0.67
Benzene	159.02	8	50.21	0.99	0.01
LP feed	57.94	1	213.30	0.33	0.67
LP distillate	57.79	1	163.51	0.38	0.62
Recycle	57.79	1	163.51	0.38	0.62
Methanol	63.47	1	49.79	0.01	0.99

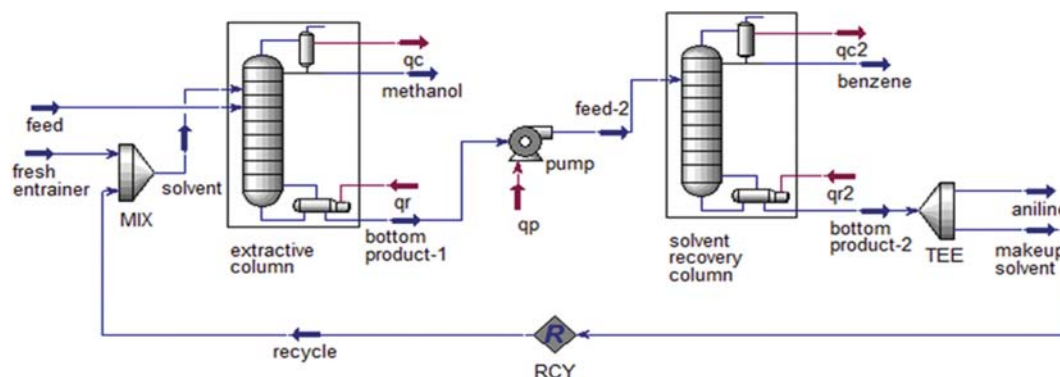


Fig. 10. Extractive distillation process flow sheet for separation of methanol and benzene with aniline as an entrainer (solvent).

the bottom along with solvent. In this work, methanol rises the top of the column and benzene, along with aniline, is collected at the bottom of the column. The bottom product is then fed to the second column, "solvent recovery column," which recovers pure solvent as the bottom product and pure benzene as distillate. The pure aniline is then recycled to the first column to mix with the fresh entrainer. Hence, in this process, pure methanol and benzene are recovered from distillate of extractive and solvent recovery column, respectively.

Optimization work is also done to minimize the important variables in extractive distillation process. Fig. 11 represents the feed and solvent stage optimization to minimize the reboiler heat duties in extractive distillation column. In Aspen HYSYS, the feed stage is not a process variable accessible to optimizer, rather it is a configurational parameter. So, it is optimized by using automation

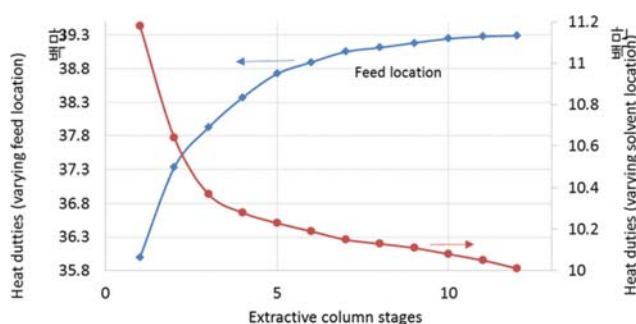


Fig. 11. Optimization for feed and solvent stage location for extractive column in extractive distillation process.

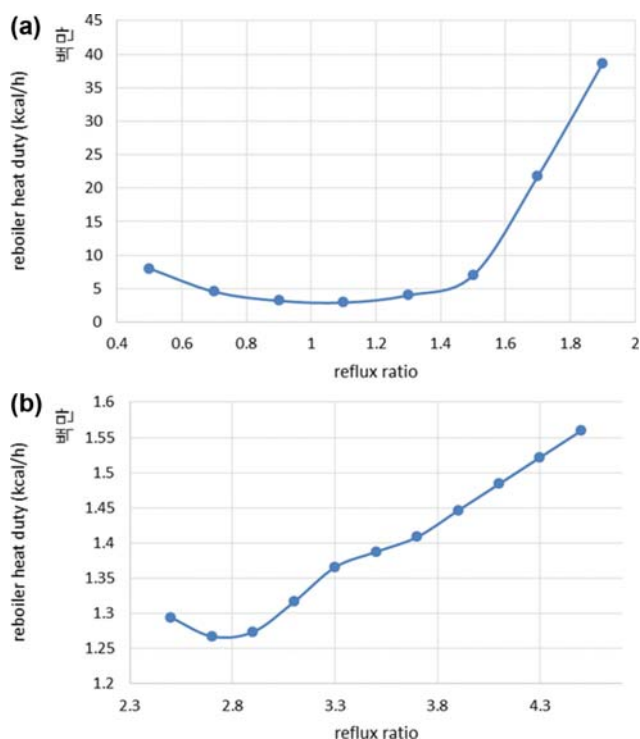


Fig. 12. Reflux ratio optimization for extractive column (a) and solvent recovery column (b) in extractive distillation process.

method to effectively modify the feed stage to a variable which is then manipulated by the optimizer. The optimization shows that the minimum heat duty is 36.00 E+06 kJ/h when feed is introduced at stage 1. In case of solvent feed location, the solvent entry at stage 12 leads to minimum reboiler heat duty, which is 10.01 E+06 kJ/h. This optimization shows that if the feed and solvent are introduced at top and bottom of the column, respectively, the maximum contact of the solvent with feed results in minimum heat duties and maximum separation. Such a large gap in feed and solvent entry stages is endorsed in previous literature as well, where it optimizes the amount of solvent used [6]. The optimized feed stage found in solvent recovery column is the 6th stage which exhibits the minimum reboiler duty of 1.67 E+06 kJ/h.

Furthermore, reflux ratio optimization was carried out for both columns, which is depicted in Fig. 12. The reflux ratio of 1.1 and 2.7 in extractive and solvent recovery column, respectively, shows the minimum energy requirement. Moreover, the effect of solvent temperature on both heat duty and methanol purity was analyzed, which is shown in Fig. 13. The heat duty of the extractive column shows an inverse relation to the temperature of the solvent, and the solvent temperature of 55 °C shows the maximum purity of methanol. The fresh solvent (entrainer) molar flow rate is another important variable which is needed to be optimized. As shown in Fig. 14, the methanol purity is maximum with fresh solvent molar flow rate of 1,700 kgmole/h. By using the optimized variables, simulation of the extractive distillation process was carried out and the results are shown in Table 3.

OPTIMIZATION ON THE BASIS OF HEAT INTEGRATION

As the pressure swing distillation process operates with two col-

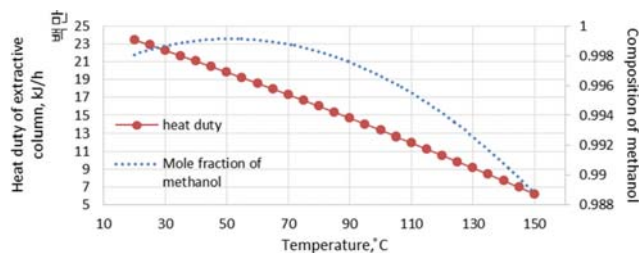


Fig. 13. Effect of fresh entrainer temperature on composition of methanol and heat duty in extractive column.

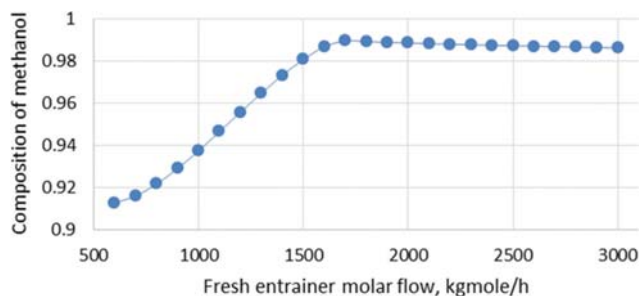


Fig. 14. Effect of fresh entrainer molar flow rate on methanol purity.

Table 3. Simulation results for extractive distillation process

	Temperature C	Pressure bar	Molar flow kgmole/h	Composition (mole fraction)		
				Benzene	Aniline	Methanol
Methanol	63.83	1	60	0.005	0.001	0.994
Feed	50	1	100	0.4	0	0.6
Fresh entrainer	55	1	1700	0	1	0
Bottom product-1	172	1	1830	0.025	0.975	0.002
Feed-2	172	1	1830	0.025	0.975	0.002
Benzene	74.59	1	25	0.980	0.005	0.015
Bottom product-2	178.6	1	1805	0.010	0.990	0
Aniline	178.6	1	1714	0.010	0.990	0
Makeup solvent	178.6	1	90.24	0.010	0.990	0
Solvent	61.83	1	1790	0.001	0.999	0
Recycle	178.5	1	89.73	0.010	0.990	0

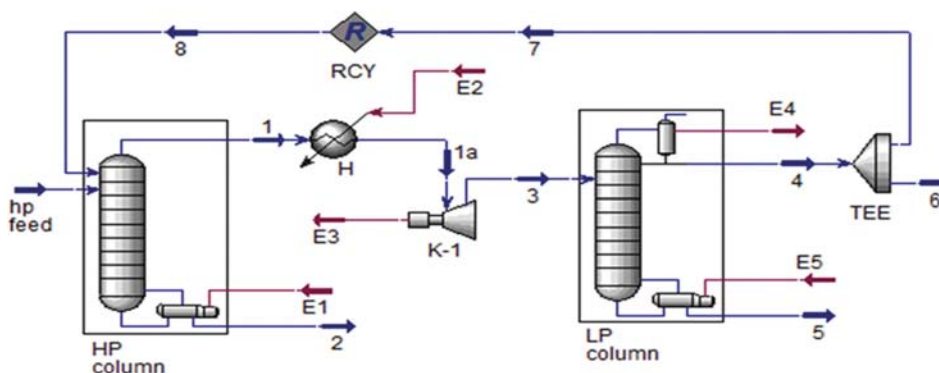
umns having different pressures, a large temperature difference is found between condenser of HP column and reboiler of LP column. Hence, this large temperature difference creates the possibility of heat integration by which the HP column heat is provided to LP column for the necessary reboil in LP column. For this purpose, heat integration based on different configurations is proposed for utilizing HP column top vapors to provide reboil energy in the bottom of the LP column. The heat integration schemes are designed for the HP-LP column sequence as, in this work, the HP-LP sequence is proved to be the optimum sequence for PSD process of benzene and methanol mixture.

Scheme 1, which is heat integrated design without omitting any reboiler, is portrayed in Fig. 15. It reduces the condenser's capital cost and cold water requirement in the HP column and the hot vapors are utilized in the LP column in the form of LP feed. As the HP column's top stream contains vapors, an expander was used instead of a pump for decreasing pressure to 1 bar. At first, the Scheme 1 was designed without any auxiliary heater, which resulted in methanol maximum purity of 82% in the LP column bottom. Therefore, the auxiliary heater was added to the process to achieve the required temperature for complete separation of methanol. Hence, Scheme 1 is a partial heat integrated design due to the presence of auxiliary heater and LP column reboiler. In this design, the reboiler heat duty in LP column is reduced to 5.21 E+05 kJ/h, which

is much lower than the one required in conventional PSD process. The auxiliary heater has a heat duty of 1.28 E+05 kJ/h, which is an extra burden over operating cost of the system and this problem was solved in Scheme 2 (Fig. 16).

The partial heat integration in Scheme 1 was further optimized by using two-way heat integration in a single configuration, which is Scheme 2. Two-way heat integration is applied by introducing HP top vapors into LP column as LP feed and by exchanging HP top vapors' heat with LP column's bottom stream. In this way, the auxiliary heater is removed from the process and the energy requirements are completely met by utilizing hot streams within the process. The successfully simulated flowsheet for this design is shown in Fig. 16. The stream 1 is split and a part of it is introduced to LP column, while the stream 3 is used to exchange its heat with LP column's bottom stream 16. The heated stream 10 is then introduced to LP column and the tube side outlet stream 5 is recycled to HP column. This heat integrated design overcomes all the energy requirements and the process is successfully converged with over 99% purity of benzene and methanol in streams 2 and 15, respectively. The reboiler heat duties in HP and LP column are reduced to 7.80 E+06 and 1.10 E+05 kJ/h, respectively. Scheme 2 shows more energy savings and, hence, it is economically more favorable than Scheme 1 (Fig. 15).

A remarkable saving in capital cost and operating cost is achieved

**Fig. 15. Partial internal heat integration of PSD process using an auxiliary heater (Scheme 1).**

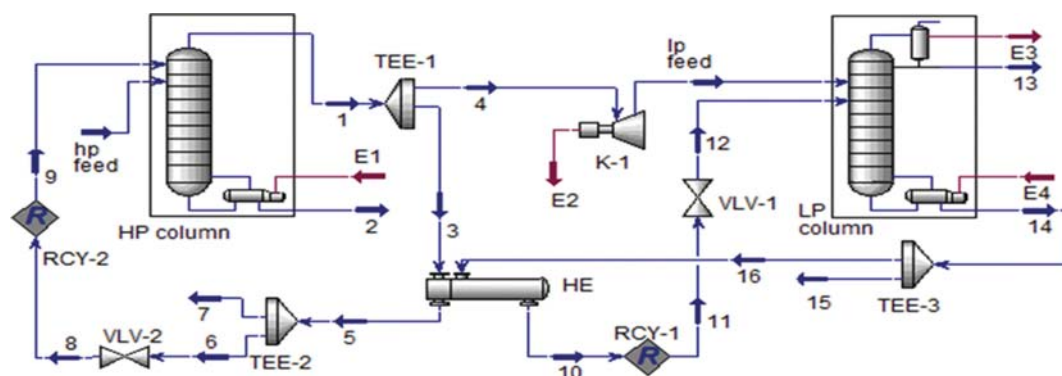


Fig. 16. Partial internal heat integration of PSD process with no auxiliary condenser or reboiler (Scheme 2).

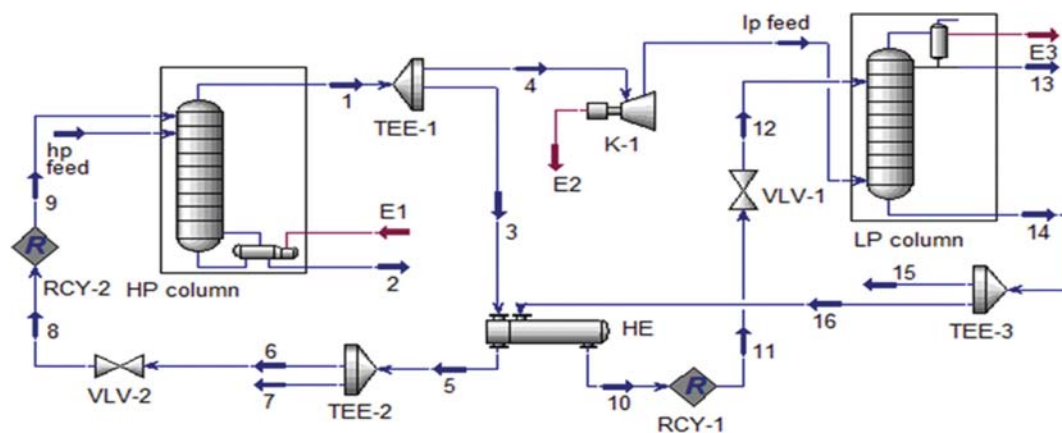


Fig. 17. Full internal heat integrated PSD process with a reboiler in HP column and a condenser in LP column (Scheme 3).

by using another unique and fully heat integrated configuration in Scheme 3 (Fig. 17). This scheme omits a condenser in the HP column and reboiler in the LP column. Hence, utility demands also undergo a tremendous fall as the newly proposed configuration makes use of only a reboiler in the HP column and a condenser in the LP column. Moreover, no auxiliary heater is required in Scheme 3. Fig. 17 shows a successfully converged simulated flowsheet of fully heat integrated PSD process which ensures 99% pure products in the bottom of both columns. In this configuration, the HP column top vapors (stream 1), with temperature 135.6 °C and pressure 8 bar, are introduced to a heat exchanger along with the LP column's bottom product stream 16. The LP column's bottom stream has temperature 63.21 °C, which can be heated enough by HP column top vapors. The heated shell side outlet stream 10 is then fed to LP column to overcome the energy requirements. The cooled tube side outlet is then introduced to HP column as the reflux stream. It can be observed in the simulated flowsheet that no auxiliary heater was added to meet energy requirements. Hence, the proposed design demystifies the most effective and economically beneficial process configuration for the separation of benzene and methanol azeotropic mixture. The streams, 2 and 15, provide ~99% benzene and methanol, respectively. Scheme 3 exploits only one reboiler in the HP column which has heat duty of 7.80 E+06 kJ/h. Fig. 18 compares the total reboiler heat duties exhibited by all processes to get pure products.

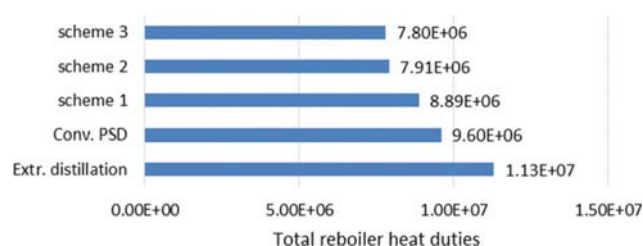


Fig. 18. Comparison of total reboiler heat duties in all processes studied.

ECONOMIC COMPARISON

Economic aspects of all the processes were analyzed using Aspen HYSYS economic analyzer and the objective function was defined. First, all equipment used in the processes was sized and mapped according to the real industrial conditions, and then the economic aspects were evaluated. An objective function was defined by a mathematical formulation, Eq. (8), so that a comprehensive comparison can be carried out on the basis of total project capital cost, total operating cost and total utilities. The objective function is defined as the summation of PCC (project capital cost), TOC (total operating cost) and CD (capital depreciation). The basis of one year operation along with required fixed project capital cost is used for objective function and the process with minimum objec-

tive function value is considered to be the most effective process. The project capital cost, defined in Eq. (9), is the summation of all expenses required for purchasing equipment and installation of industrial operations along with contingency cost. TOC, expressed in Eq. (10), is total cost required for operation constituting utilities cost, operating labor and maintenance costs. CD shows the capital cost of equipment along with depreciation factor and is defined in Eq. (11).

$$\text{Objective Function} = \text{Min. [PCC} + \text{TOC} + \text{CD}] \quad (8)$$

$$\text{PCC} = \sum_i C_{i(\text{total capital})} \quad (9)$$

$$\text{TOC} = \sum_i C_{i(\text{total operating})} \quad (10)$$

$$\text{CD} = \sum_i C_{i(\text{equipment})} D \quad (11)$$

The economic evaluation of conventional PSD, extractive distillation process and heat integrated PSD schemes unveils the process with minimum and optimized objective function. A process with minimized objective function will certainly exhibit a higher profit. It can be observed that the reboilers in HP columns in PSD and extractive column in extractive distillation utilize the highest amount of utilities. Conventional PSD, comparatively, seems economically attractive as it requires less steam and electricity than extractive distillation process. Additional savings are also possible by using the heat integration in PSD. The cost for steam and cooling water utilized in PSD is 142.61 and 10.20 USD/h, respectively, and the cost of steam and cooling water exhibited by extractive distillation is 514.79 and 8.35 USD/h, respectively. PSD Scheme 3 shows maximum savings, and the cost of steam and cooling water is found to be 84.90 and 4.81 USD/h, respectively. The objective function for all processes is demystified in Fig. 19. Fully heat integrated PSD exhibits a minimized objective function, 6.10 E+06 USD, which is economically more favorable than that of Scheme 1 (6.65 E+06), Scheme 2 (6.73 E+06), conventional PSD (7.41 E+06 USD) and extractive distillation (9.79 E+06 USD).

Fig. 20 expresses PCC, TOC and total utilities consumed for all processes. It can be analyzed in economic comparison that PSD requires remarkably less capital and operating cost to industrially separate the azeotropic mixture of benzene and methanol. Total proj-

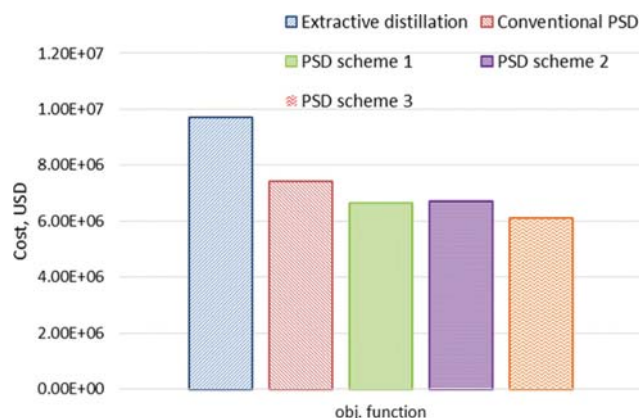


Fig. 19. Comparison of objective function for extractive distillation, conventional PSD and heat integrated PSD schemes.

ect capital cost and total operating costs for conventional PSD are 4.19 E+06 USD and 2.47 E+06 USD/year, respectively, and the depreciation expense calculated by straight line method is 7.50 E+05 USD/year. Among the heat integrated schemes, fully heat integrated Scheme 3 shows a maximum fall in the utility demand and the total project capital and operating costs are calculated to be 3.89 E+06 USD and 1.47 E+06 USD/year, respectively, with the depreciation expense of 7.35 E+05 USD/year. Hence, PSD Scheme 3 ensures a saving of 2.99 E+05 USD in capital cost and 9.95 E+05 USD/year in operating cost while using PSD process.

CONCLUSION

The separation of methanol and benzene azeotropic mixture has been studied with rigorous simulations of pressure swing distillation and extractive distillation. Pressure swing distillation process has been carried out with two different column sequences, and the optimization of variables denotes that the HP-LP column sequence is the most optimum column sequence for separation of methanol and benzene. PSD process has been proven economically more attractive than extractive distillation. Moreover, the possibility of heat integration is the special feature of PSD process which makes it

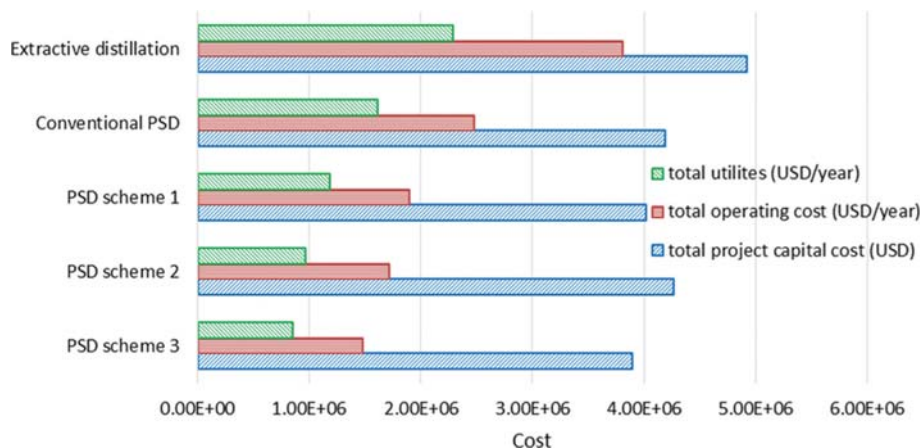


Fig. 20. Economic comparison of all processes on the basis of total project capital cost, total operating cost and total utilities.

advantageous over extractive distillation. PSD process has been further optimized by heat integration. The newly proposed configuration of full internal heat integration, with HP-LP column sequence, is the most optimum process and compared to conventional PSD process, it provides 9.95 E+05 USD/year saving in total operating cost. Hence, pressure swing distillation with full internal heat integration is economically more favorable for separation of azeotropic mixtures. This study provides optimum process conditions for all studied processes, and the internal heat integrated PSD process is found to be the most promising process.

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